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# Hydrothermal syntheses and structural characterization of four complexes with *in situ* formation of 1,2,3-triazole-4-carboxylate ligand

Ze-Bao Zheng<sup>a,\*</sup>, Ren-Tao Wu<sup>a</sup>, Ji-Kun Li<sup>b</sup>, Yi-Feng Sun<sup>a</sup>

<sup>a</sup> Department of Chemistry and Environmental Science, Taishan University, Yingbin Street, Taian, Shandong 271021, PR China <sup>b</sup> Department of Materials and Chemical Engineering, Taishan University, Taian, Shandong 271021, PR China

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# ABSTRACT

Four new complexes constructed by 1,2,3-triazole-4-carboxylate and bipyridyl-like ligands, namely  $[Cu(ta)(bipy)\cdot H_2O]_n$  (1),  $[Mn_2(ta)_2(bipy)_2(H_2O)_2\cdot 2H_2O]_n$  (2),  $[Zn(ta)(phen)_2\cdot 5H_2O]_n$  (3),  $[Ni(ta)(phen)_2\cdot 8H_2O]_n$  (4), (ta = 1,2,3-triazole-4-carboxylate, bipy = 2,2'-bipyridine, phen = 1,10-phen) were prepared under hydrothermal conditions and characterized by IR, elemental analyses and single-crystal X-ray analyses. Where the ta ligand is formed *in situ* by the decarboxylation of 1*H*-1,2,3-triazole-4,5-dicarboxylic acid. In the complex 1, the Cu (II) ions are bridged by ta ligand into a one-dimensional zigzag chain coordination polymer motif. Binuclear  $[Mn_2(ta)_2(bipy)_2(H_2O)_2]$  units bridged by ta ligands are linked into a two-dimensional layered structure *via* interdimeric hydrogen bonds within the structure of 2. Compounds 3 and 4 are connected *via* intermolecular O—H…O hydrogen bonds into 1D tapes and 2D layers, respectively.

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# 1. Introduction

The synthesis and construction of metal–organic coordination polymers have been rapidly developed in the recent decades due to their interests in both structural diversities and potential applications as functional materials [1], such as magnetism, host–guest chemistry, catalysis, and functional porous materials [2,3]. Some weak interactions, such as hydrogen-bonding and  $\pi$ – $\pi$  stacking interactions, also greatly affect the structures of coordination complexes [4]. Moreover, they may link low-dimensional entities into high-dimensional supramolecular networks [5].

More recently, hydro(solvo)thermal *in situ* ligand reactions have provoked significant interest in not only the discovery of new organic reactions but also the exploration of uncommon metalorganic frameworks (MOFs) that exhibit intriguing structural diversity and/or promising properties for potential applications [6–9]. Especially, some functional coordination polymers that are inaccessible or not easily obtainable by routine synthetic methods can also be obtained by hydro(solvo)thermal *in situ* ligand reactions. Up to now, carbon–carbon bond formation [10–11], oxidative hydroxylation of aromatic rings [12–13], decarboxylation of aromatic carboxylates [14–15], hydrolysis of carboxylate esters or organic nitriles [16], cycloaddition of organic nitriles with azide or ammonia [17–18], cleavage and formation of disulfide bonds [19–21] and many other hydro(solvo)thermal *in situ* ligand reactions have been successfully utilized to obtain new coordination polymers. To the best of our knowledge, the coordination chemistry and structural properties of metal polymers containing ta ligands have been seldom documented to date [22]. In this contribution, we report the preparation, X-ray crystal structures and properties of four new coordination polymers: [Cu(ta) (bipy)·H<sub>2</sub>O]<sub>n</sub> (1), [Mn<sub>2</sub>(ta)<sub>2</sub>(bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2H<sub>2</sub>O]<sub>n</sub> (2), [Zn(ta)(phen)<sub>2</sub>·5H<sub>2</sub>O]<sub>n</sub> (3), [Ni(ta)(phen)<sub>2</sub>·8H<sub>2</sub>O]<sub>n</sub> (4). The 1,2,3-triazole-4-carboxylate is formed from the 1*H*-1,2,3-triazole-4,5-dicarboxylic acid precursor *via in situ* decarboxylation under hydrothermal conditions.

#### 2. Experimental

#### 2.1. Materials and methods

All reagents and solvents employed were commercially available and used as received without further purification. H<sub>3</sub>tda was synthesized according to the literature method [23].

Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs. Thermogravimetric analysis (TGA) was carried out on a Delta Series TA-SDTQ600 in nitrogen atmosphere from room temperature to 800 °C (heating rate = 10 °C min<sup>-1</sup>) using aluminium crucibles. Elemental analyses were performed with a PE-2400II apparatus.



<sup>\*</sup> Corresponding author. Tel./fax: +86 538 6710865.

E-mail address: zhengzebao@163.com (Z.-B. Zheng).

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#### 2.2. Syntheses

[Cu(ta)(bipy)·H<sub>2</sub>O]<sub>n</sub> (1): A mixture of Cu(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.109 g, 0.5 mmol), H<sub>3</sub>tda (0.078 g, 0.5 mmol) and 2,2'-bipy (0.082 g, 0.5 mmol) was dissolved in water (12 ml) and ethanol (3 ml). The pH of the solution was adjusted to be about 6–7 with 0.2 mol L<sup>-1</sup> aqueous NaOH, then the mixed solution was stirred for 30 min at room temperature, transferred to and sealed in a 25 ml Teflon-lined stainless steel reactor, and then heated at 150 °C for 72 h. Upon cooling to room temperature, a blue solution was filtered and the filtrate was allowed to stand at room temperature. After slow evaporation over three weeks, blue block single crystals were obtained. Yield: 32% based on Cu. *Anal.* Calcd. for C<sub>13</sub>H<sub>11</sub>CuN<sub>5</sub>O<sub>3</sub>: C, 44.76; H, 3.18; N, 20.07. Found: C, 44.71; H, 3.14; N, 20.14. IR (KBr, cm<sup>-1</sup>): 3385 (s), 1588 (s), 1531 (m), 1424 (s), 1373 (m), 1285 (w), 871 (m), 722 (s).

 $[Mn_2(ta)_2(bipy)_2(H_2O)_2\cdot 2H_2O]_n$  (2): The hydrothermal procedure for the synthesis of complex 2 is similar to that for 1 except that with the replacement of Cu(CH\_3COO)\_2\cdot 2H\_2O with MnCl\_2\cdot 4H\_2O (0.099 g, 0.5 mmol), light yellow crystals were obtained. Yield: 35% based on Mn. *Anal.* Calcd. for C<sub>26</sub>H<sub>26</sub>Co<sub>2</sub>N<sub>10</sub>O<sub>8</sub>: C, 43.58; H, 3.66; N, 19.54. Found: C, 43.52; H, 3.61; N, 19.60. IR (KBr, cm<sup>-1</sup>): 3386 (s), 1598 (s), 1518 (m), 1429 (s), 1382 (m), 1193 (w), 809 (m), 773 (s).

 $[Zn(ta)(phen)_2 \cdot 5H_2O]_n$  (3): A mixture of  $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.110 g, 0.5 mmol), H<sub>3</sub>tda (0.078 g, 0.5 mmol) and phen (0.206 g, 1.0 mmol) was dissolved in water (12 ml) and ethanol (3 ml). The pH of the solution was adjusted to be about 6–7 with 0.2 mol L<sup>-1</sup> aqueous NaOH, then the mixed solution was stirred for 30 min at room temperature, transferred to and sealed in a 25 ml Teflonlined stainless steel reactor, and then heated at 150 °C for 72 h. Upon cooling to room temperature, a colorless solution and a small amount of white precipitate were obtained. The solution was filtered and the filtrate was allowed to stand at room temperature. After slow evaporation over three days, colorless block single crystals were obtained. Yield: 52% based on Zn. Anal. Calcd. for

Table 1

Crystal, data collection and structure refinement parameters for complexes 1-4.

 $C_{27}H_{27}ZnN_7O_7;\ C,\ 51.72;\ H,\ 4.34;\ N,\ 15.63.$  Found: C, 51.68; H, 4.30; N, 15.67. IR (KBr,  $cm^{-1});\ 3411$  (s), 1589 (s), 1526 (m), 1444 (s), 1337 (m), 1255 (w), 799 (m), 747 (s).

[Ni(ta)(phen)<sub>2</sub>·8H<sub>2</sub>O]<sub>*n*</sub> (**4**): The hydrothermal procedure for the synthesis of complex **4** is similar to that for **3** except that with the replacement of  $Zn(CH_3COO)_2 \cdot 2H_2O$  with Ni(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.107 g, 0.5 mmol) light purple crystals were obtained. Yield: 35% based on Ni. *Anal.* Calcd. for C<sub>27</sub>H<sub>33</sub>NiN<sub>7</sub>O<sub>10</sub>: C, 47.98; H, 4.93; N, 14.51. Found: C, 47.92; H, 4.98; N, 14.46. IR (KBr, cm<sup>-1</sup>): 3277(s), 1593(s), 1516 (m), 1419(s), 1357(m), 1226(w), 826 (m), 727 (s).

# 2.3. X-ray crystallography

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X-ray diffraction measurements were carried out at 295 K with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker APEX-II area-detector. A semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against  $F^2$  by full matrix least-squares using SHELXL-97 [24]. In the case of **4**, the all-data *R*-factors are not ideal, which may be attributed to the quality of the crystal and to the high degree of hydration and thermal motion. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1. Selected bond lengths and angles for complexes **1–4** are summarized in Table 2.

# 3. Results and discussion

# 3.1. Syntheses

1*H*-1,2,3-Triazole-4,5-dicarboxylic acid and bipyridyl-like mixed ligands were reacted in aqueous-ethanol medium with different metal salts (Cu(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O) at pH ranging from 6 to 7 in an attempt to investigate the reactivity. Surprisingly, the results of

Complex	1	2	3	4
Empirical formula	$C_{13}H_{11}CuN_5O_3$	$C_{26}H_{26}Mn_2N_{10}O_8$	C <sub>27</sub> H <sub>27</sub> Zn N <sub>7</sub> O <sub>7</sub>	C <sub>27</sub> H <sub>33</sub> Ni N <sub>7</sub> O <sub>10</sub>
Formula weight	348.81	716.45	626.93	674.32
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	Pbca	PĪ	P2(1)/c	PĪ
a (Å)	16.108(2)	8.830(6)	10.530(8)	10.446(1)
b (Å)	9.363(1)	9.454(7)	25.658(2)	11.104(1)
c (Å)	18.88(2)	9.536(7)	10.698(8)	14.869(1)
α (°)	90	98.657(1)	90	81.703(2)
β(°)	90	101.115(1)	107.676(1)	72.757(2)
γ (°)	90	101.790(1)	90	72.69(2)
Ζ	8	1	4	2
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.627	1.587	1.512	1.429
F(000)	1416	366	1296	706
$\mu (\mathrm{mm}^{-1})$	1.554	0.909	0.952	0.683
Crystal size (mm)	$0.18 \times 0.16 \times 0.12$	$0.15\times0.12\times0.10$	$0.18 \times 0.16 \times 0.12$	$0.18 \times 0.16 \times 0.10$
θ range (°)	2.16-25.05	2.22-25.04	1.59-25.05	1.44-25.04
Index ranges	$-19 \leqslant h \leqslant 19;$	$-10 \leqslant h \leqslant 10;$	$-12\leqslant h\leqslant 12;$	$-12\leqslant h\leqslant 10$ ,
	$-9 \leqslant k \leqslant 11;$	$-7 \leqslant k \leqslant 11;$	$-29 \leqslant k \leqslant 30;$	$-13 \leqslant k \leqslant 11$ ,
	$-22 \leqslant l \leqslant 14$	$-11 \leq l \leq 11$	$-10 \leqslant l \leqslant 12$	$-16 \leqslant l \leqslant 17$
Reflections collected	13,097	3996	14,428	7768
Unique reflections	2517	2641	4875	5416
	$(R_{\rm int} = 0.1401)$	$(R_{\rm int} = 0.0171)$	$(R_{\rm int} = 0.0488)$	$(R_{\rm int} = 0.0848)$
Data/restraints/parameters	2517/0/199	2641/0/208	4875/0/379	5416/0/406
Goodness of fit on F <sup>2</sup>	1.038	1.041	1.039	1.068
Final <i>R</i> indices $[I > 2\sigma(I)]$	<i>R</i> 1 = 0.0599, <i>wR</i> 2 = 0.1421	R1 = 0.0322, wR2 = 0.0703	R1 = 0.0630, wR2 = 0.1468	<i>R</i> 1 = 0.0944, <i>wR</i> 2 = 0.1734
R indices (all data)	<i>R</i> 1 = 0.1347, <i>wR</i> 2 = 0.1938	<i>R</i> 1 = 0.0412, <i>wR</i> 2 = 0.0751	<i>R</i> 1 = 0.0971, <i>wR</i> 2 = 0.1674	<i>R</i> 1 = 0.2972, <i>wR</i> 2 = 0.2428
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.014/-0.356	0.234/-0.228	1.446/-0.647	0.517/-0.493

Table	2
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Selected be	ond lengths	(Å)	and	angles (	°) f	or com	plexes	1-4	ł.

Compound <b>1</b>			
Cu(1)—N(3)#1	1.983(6)	Cu(1)—N5	2.019(7
Cu(1) - N(4)	2.009(6)	Cu(1)-N1	2.174(6
Cu(1) - O(1) # 1	2.013(6)		
N(3)#1-Cu(1)-N(4)	166.5(2)	O(1)#1-Cu(1)-N(5)	160.6(2
N(3)#1-Cu(1)-O(1)#1	82.4(2)	N(3)#1-Cu(1)-N(1)	94.3(2)
N(4) - Cu(1) - O(1) #1	92.0(2)	N(4) - Cu(1) - N(1)	98.8(3)
N(3) #1 - Cu(1) - N(5)	1004(3)	O(1)#1-Cu(1)-N(1)	100 7(2
N(4) - Cu(1) - N(5)	81 0(2)	N(5) - Cu(1) - N(1)	98 2(2)
	01.0(2)		50.2(2)
Compound 2	2147(2)		2 22 4/2
V(n(1) - O(3))	2.147(2)	Mn(1) - N(5)	2.234(2
Mn(1) - N(2) # 2	2.202(2)	Mn(1) - O(1)	2.242(2
Mn(1) - N(1)	2.220(2)	Mn(1) - N(4)	2.266(2
O(3) - Mn(1) - N(2) #2	89.3(7)	N(1) - Mn(1) - O(1)	74.4(6)
O(3) - Mn(1) - N(1)	93.7(7)	N(5) - Mn(1) - O(1)	93.4(7)
N(2)#2-Mn(1)-N(1)	97.9(7)	O(3) - Mn(1) - N(4)	168.9(7
O(3) - Mn(1) - N(5)	97.3(7)	N(2)#2-Mn(1)-N(4)	96.9(7)
N(2)#2-Mn(1)-N(5)	95.0(7)	N(1) - Mn(1) - N(4)	94.5(7)
N(1) - Mn(1) - N(5)	163.1(7)	N(5) - Mn(1) - N(4)	73.1(7)
O(3) - Mn(1) - O(1)	87.1(6)	O(1) - Mn(1) - N(4)	87.9(7)
N(2)#2-Mn(1)-O(1)	171.3(6)		
Compound <b>3</b>			
Zn(1)-N(1)	2.084(6)	Zn(1)—N(5)	2.174(4
Zn(1)—N(7)	2.130(4)	Zn(1)—N(6)	2.187(4
Zn(1)—N(4)	2.149(4)	Zn(1)-O(1)	2.241(5
N(1) - Zn(1) - N(7)	98.8(2)	N(5) - Zn(1) - N(6)	97.0(2)
N(1) - Zn(1) - N(4)	95.6(2)	N(1) - Zn(1) - O(1)	77.6(3)
N(7) - Zn(1) - N(4)	164.1(2)	N(7) - Zn(1) - O(1)	91.2(2)
N(1) - Zn(1) - N(5)	102.3(2)	N(4) - Zn(1) - O(1)	98.4(2)
N(7) - Zn(1) - N(5)	93.4(2)	N(5) - Zn(1) - O(1)	175.3(2
N(4) - Zn(1) - N(5)	77.0(2)	N(6) - Zn(1) - O(1)	83.4(2)
N(1) - Zn(1) - N(6)	160.6(2)	N(7) - Zn(1) - N(6)	77.5(2)
N(4) - Zn(1) - N(6)	91.1(2)		. ,
Compound <b>4</b>			
Ni(1) - N(1)	2.044(1)	Ni(1) - N(6)	2 090(8
Ni(1) - N(5)	2.011(1) 2.088(8)	Ni(1) - N(7)	2.000(8
Ni(1) - N(4)	2.000(8)	Ni(1) - O(1)	2.035(0
N(1) - Ni(1) - N(5)	101.0(5)	N(4) - Ni(1) - O(1)	92 5(3)
N(1) - Ni(1) - N(4)	95.0(3)	N(6) - Ni(1) - O(1)	85 6(3)
N(5) - Ni(1) - N(4)	79.6(4)	N(7) - Ni(1) - O(1)	938(3)
N(1) - Ni(1) - N(6)	161.8(4)	N(4) = Ni(1) = N(7)	171 0/2
N(5) - Ni(1) - N(6)	101.0(4)	$N(-1)^{-1}N(1)^{-1}N(7)$	20 1(4)
N(J) = NI(1) = N(0) N(J) = NI(1) = N(6)	90.2(3)	N(0) = N(1) = N(7) N(1) = N(1) = O(1)	00.1(4) 78.2(5)
N(4) = N(1) = N(0)	93.9(3)	N(1) = N(1) = O(1) N(5) = N(1) = O(1)	/ 8.2(5)
N(1) - N(1) - N(7)	92.0(3)	N(3) - NI(1) - O(1)	172.0(3
N(5) - NI(1) - N(7)	94.2(3)		

Symmetry transformations used to generate equivalent atoms: #1 - x + 1/2, y - 1/2, z; #2 - x, -y + 2, -z.

single-crystal structural analysis indicate that the metal atoms in those complexes are coordinated by ta ligands, rather than the deprotonated species of  $H_3$ tda. This means that the *in situ* decarboxylation from  $H_3$ tda to ta occurred under the hydrothermal conditions.

# 3.2. Description of crystal structures

#### 3.2.1. $[Cu(ta)(bipy) \cdot H_2O]_n$ (1)

The coordination environment of the Cu(II) ion in complex **1** is shown in Fig. 1. The Cu(II) ion is five coordinated, with one oxygen atom from a ta ligand, two nitrogen atoms from one 2,2'-bipy ligand and two nitrogen atoms from two ta ligands. The Cu(II) atom exhibits a distorted square-pyramidal environment with the atoms N4, N5, O1A, and N3A in the basal plane and N1 in the apical position. The Cu—N bond lengths are 1.983(6) to 2.174(6) Å, and the Cu—O bond length is 2.013(6) Å. The Cu1—N1 and Cu1—O1 bond distances are comparable to those reported for Cu(H<sub>2</sub>tda)(H<sub>2</sub>O)<sub>4</sub> [22]. In complex **1**, every ta ligand adopts a tridentate mode (Scheme 1a), as shown in Fig. 2, each Cu(II) atom is joined to an-



**Fig. 1.** View of the metal coordination environment in **1** (H atoms and lattice water are omitted for clarity).

other one by a ta ligand with the distance of 6.192(2) Å and forms a 1D zigzag chain along the *b*-axis.

# 3.2.2. $[Mn_2(ta)_2(bipy)_2(H_2O)_2 \cdot 2H_2O]_n$

As shown in Fig. 3, two neighboring Mn(II) ions are bridged by two 1,2,3-triazole-4-carboxylate groups, forming a binuclear structure with the distance between Mn1 and Mn1A being 0.4230 nm. Each Mn(II) coordinates with two nitrogen atoms from one bipy molecule, one oxygen atom and two nitrogen atoms from two ta ligands and one oxygen atom from one water molecule, to give a six-coordinate distorted octahedral structure, in which the equatorial plane is formed by N1, N4, N5 and O3 with a mean deviation of 0.0546 Å from the least-squares plane. The axial positions are occupied by O1 and N2A with an O1–Mn1–N2A angle of 171.3(6)°.

In complex **2**, the ligand exhibits a tridentate binding mode (modes (b) in Scheme 1), differing from that in complex **1**. In addition, the coordinated water molecules are connected with ta groups through multiple strong hydrogen bonds (Table 3), which generate a two-dimensional layered structure (Fig. 4).

# 3.2.3. [Zn (ta) (phen)<sub>2</sub>·5H<sub>2</sub>O]<sub>n</sub> (**3**) and [Ni(ta)(phen)<sub>2</sub>·8H<sub>2</sub>O]<sub>n</sub> (**4**)

The crystal analysis of complex **3** reveals that it is a monouclear complex consisting of one Zn (II) ion, two phen molecules and one 1,2,3-triazole-4-carboxylate anion. The Zn (II) center exhibits a distorted octahedral surrounding (Fig. 5), in which the equatorial plane is formed by two nitrogen atoms (N5, N6) from two phen molecules and two atoms (N1, O1) from a ta anion with a mean deviation of 0.0743 Å from the least-squares plane. The axial positions are occupied by two nitrogen atoms (N4, N7) from two phen molecules with an N4–Zn1–N7 angle of 164.14(16)°. The ta ligand exhibits a bidentate binding mode (modes (c) in Scheme 1).

Interestingly, the five crystal-lattice water molecules and their equivalents are interlinked by O—H…O hydrogen bonds into 1D infinite tapes in the *c* direction (Fig. 6a). The geometric parameters of the hydrogen bonds are summarized in Table 4. The average O…O distance of 2.84 Å is longer than that of 2.78 Å estimated in the tetramer of  $(D_2O)_4$  [25], however, it is comparable to the corresponding value of 2.85 Å in liquid water [26], and other examples of 1D water tapes [27–28]. The water tapes consist of fused four-



Scheme 1. The coordination mode of ta.



Fig. 2. The 1D zigzag chain structure of 1 viewed along the *b*-axis.



Fig. 3. View of the metal coordination environment in 2 (H atoms and lattice water are omitted for clarity).

Table 3The hydrogen bonds in complex 2.

D—H…A	<i>d</i> (D—H)	<i>d</i> (H…A)	<i>d</i> (D···A)	∠(DHA
03—H14…01#1	0.85	1.91	2.76	172.09
03—H15…O4#1	0.85	1.89	2.72	164.33
04—H17…O2#2	0.85	1.92	2.73	159.80
04—H16…O2	0.85	2.11	2.89	153.35

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y + 2, -z; #2 -x + 1, -y + 1, -z.

and five-membered water rings, resulting in a water cluster notation as T4(2)5(2) according to Infantes' classification [29]. The tapes are linked by  $Zn(tac)(phen)_2$  units through O—H…O and O—H…N hydrogen bonded to form a 2D supramolecular layer (Fig. 6b).

The molecular structures of complexes **3** and **4** are similar (The molecular structure of compound **4** is shown in Fig. 7). However, the numbers of crystal-lattice water molecules in both complexes are different, five water molecules for **3** and eight water molecules for **4**, respectively. In the formation of water cluster for compound **4** these results differ from those of compound **3**.



**Fig. 4.** Perspective view of the 2D supramolecular layer of complex **2**, the C atoms of bipy ligands and H atoms are omitted for clarity.



Fig. 5. Molecular structure of complex 3 with 30% probability ellipsoids, hydrogen atoms are omitted for clarity.

Most interestingly, in **4** the water molecules formed two types of water clusters (Fig. 8a): a 1D water tape consisting of fused fourand ten-membered water rings formed by O6A, O7A, O8A, O9A, O10A and their equivalents with the notation T4(2)10(2); hexamer formed by O3A, O4A, O5A and their equivalents. The 1D tapes were connected to the hexamers by hydrogen bonding into an unusual 2D layered notation as L4(4)6(2)10(6)20(10) according to Infantes' classification [29] (Fig. 8a). The average O…O distance of 2.82 Å is







(b)

**Fig. 6.** (a) The 1D infinite chains formed by the crystal-lattice water molecules in complex **3** *via* intermolecular O–H…O hydrogen bonds. (b) Perspective view of the 2D supramolecular layer of complex **3**, the C atoms of phen and H atoms are omitted for clarity.

Table 4

The hydrogen bonds in complex 3.

D—H…A	d(D—H)	d(H…A)	d(D…A)	∠(DHA)
03—H26…O1	0.85	1.99	2.83	172.65
03-H2706#1	0.85	2.00	2.83	165.98
04—H29…N3#2	0.85	2.01	2.83	162.74
04–H28…O2	0.85	1.87	2.72	175.19
05–H30…O4	0.85	1.98	2.82	173.50
05—H31…O3#3	0.85	2.04	2.88	172.46
06–H33…07	0.85	2.05	2.87	161.30
06—H32…O4#3	0.85	1.94	2.78	172.78
07—H34…O5	0.85	2.00	2.83	164.24
07—H35…O3#4	0.85	2.01	2.85	169.14

Symmetry transformations used to generate equivalent atoms: #1 x, -y + 1/2, z + 1/2; #2 -x + 1, -y, -z + 1; #3 x, -y + 1/2, z - 1/2; #4 x, y, z - 1.

longer than that of 2.78 Å in the 2D  $(H_2O)_8$  rings in [Cu(H-mal)(4pds)]·6H<sub>2</sub>O [30], and very close to the corresponding value of 2.84 Å in complex **3**. The 2D water network is interpenetrated with Ni(tac)(phen)<sub>2</sub> units through O–H…O hydrogen bonds into a 3D supramolecular network (Table 5 and Fig. 8b).



**Fig. 7.** Molecular structure of complex **4** with 30% probability ellipsoids, hydrogen atoms and lattice water are omitted for clarity.

Table 5				
The hydrogen	bonds	in	complex	4

D—H…A	d(D-H)	d(H…A)	d(D…A)	∠(DHA)
03—H27…O5	0.85	2.26	2.79	120.67
04—H28…O3#1	0.84	2.11	2.73	130.65
04—H29…010	0.85	2.56	2.97	110.75
05—H30…O3	0.85	2.26	2.79	120.30
05—H31…O2#2	0.85	2.22	2.86	132.74
06—H33…09#3	0.85	2.10	2.82	142.25
07—H34…O2#2	0.86	2.14	2.77	129.69
07—H35…08	0.85	1.99	2.58	125.96
07—H35…08#3	0.85	2.51	3.04	121.81
08—H37…O7#3	0.85	2.38	3.04	135.14
09—H39…O6#4	0.85	2.25	2.82	124.17
09—H38…08	0.85	2.14	2.83	137.17
010-H4107	0.86	1.77	2.53	147.42
010-H4004	0.85	2.14	2.97	168.29
03—H3…O5#5	0.86	1.91	2.74	164.08

Symmetry transformations used to generate equivalent atoms: #1 - x + 1, -y + 1, -z; #2 x + 1, y, z; #3 - x + 1, -y + 1, -z + 1; #4 x, y + 1, z; #5 - x + 1, -y + 1, -z.

#### 3.3. IR spectrum and thermal stability analysis

The absence of any strong bands around  $1700 \text{ cm}^{-1}$  in the IR spectrum of **1–4** indicates that 1,2,3-triazole-4-carboxylates have been completely deprotonated in the form of ta anions. The sharp bands in the region 1598–1588 cm<sup>-1</sup> in complexes **1–4** may be attributed to the COO<sup>-</sup> asymmetric stretching modes, and the bands at 1382–1337 cm<sup>-1</sup> are characteristic of the symmetric stretching modes of COO<sup>-</sup>. The corresponding  $\Delta(v_{as} - v_s)$  data are 215 for **1**, 216 for **2**, 252 for **3** and 236 for **4**. The separation between  $v_{asym}(OCO)$  and  $v_{sym}(OCO)$  indicates the presence of monodentate coordination mode for the carboxylate group of ta anions [31]. These conclusions are also supported by the results obtained from X-ray diffraction measurements.

Thermogravimetric analysis (TGA) for compounds **1–4** was performed under a flow of N<sub>2</sub> gas (Fig. 9). For compound 1, its TG curve shows two main steps of weight losses. The first step started at 40 °C and completed at 70 °C, which corresponds to the release of one crystal-lattice water molecule. The observed weight loss of



(a)



(b)

**Fig. 8.** (a) Perspective view of the 2D supramolecular layer consisting of hydrogen bonded water molecules in complex **4**. (b) Perspective view of the 3D supramolecular networks of complex **4**, the C atoms of phen and H atoms are omitted for clarity.

5.87% is close to the calculated value (5.16%). The final step (276–310 °C) corresponds to the release of bipy and ta ligands, giving copper oxides as the final decomposition product which constitutes 23.46% (calcd. 22.80%). TG curve of **2** exhibits three steps of

weight losses. The weight loss of 12.64% during the first and second steps from 40 to 200 °C corresponds to the loss of two crystal-lattice water molecules and two coordination water molecules (calcd. 10.05%). The third step (360–420 °C) corresponds to the release of bipy and ta ligands, giving MnO as the final decomposition product which constitutes 22.56% (calcd. 21.48%).

Compound **3** loses lattice water in the range  $35-100 \,^{\circ}$ C with a weight loss of 15.30% (calcd. 14.17%). The phen ligands are released in 280–320  $^{\circ}$ C with a weight loss of 56.27% (calcd. 57.49%), resulting in the formation of an intermediate product [Zn(ta)]. This intermediate species is further decomposed in  $400-600 \,^{\circ}$ C with the formation of a final ZnO residue (found 11.59%, calcd. 12.98%). Compound **4** loses lattice water (found 18.42%, calcd. 21.48%) from 35 to  $80 \,^{\circ}$ C. The phen ligand is released in  $350-400 \,^{\circ}$ C with a weight loss of 52.16% (calcd. 53.45%). The intermediate product [Ni(ta)] is further decomposed in  $420-550 \,^{\circ}$ C with the formation of a possible final NiO residue (found 9.85%, calcd. 11.08%).

#### 4. Conclusions

In summary, we have demonstrated that the *in situ* decarboxylation from 1H-1,2,3-triazole-4,5-dicarboxylic acid to 1,2,3-triazole-4-carboxylate can occur under the hydrothermal conditions, and four metal–organic compounds with 1D chains (1), 0D dimers (2) and 0D monometer (3 and 4) structures. Most interestingly, the crystal-lattice water molecules extend those complexes into 2D (2 and 3) and 3D (4) structures by hydrogen bonds.

#### 5. Supplementary material

Crystallographic data (excluding structure factors) for the structure analyses of complexes **1–4** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 711696 **1**, 711697 **2**, 690417 **3** and 685192 **4**. Copies of these information may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Fig. 9. TG curves of compounds 1-4.

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